Gas-Volumetric Analysis of Carbonates

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Suekichi ABE and Bi SHIMA

The Chemical Research Institute of Non-Aqueous Solutions

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Synopsis

Correction values to be used on the gas-volumetric analysis of carbonates have been studied. The water vapor tension on the system, Na_2SO_4–H_2SO_4–H_2O (total SO_4: 30%) and the solubility of carbon dioxide in the system were measured and these values were applied to the analysis of carbonates. The results have proved to be in good coincidence.

I. Introduction

The industrial gas-volumetric analysis of carbonates, especially of soda ash is performed easily and promptly, which, however, requires proper corrections. The main part of the correction depends on the vapor pressure of sulfuric acid solution and the amount of carbon dioxide dissolved in the solution. There have been some propositions on the correction[1], but they were not sufficient. As the correction value to be applied to such volumetric analysis varies according to the analytical condition and the composition of the sample and others, it is necessary to know correct values of vapor pressure of the solution and the solubility of the gas extending to wide range. These values have been measured as they were not found in the literature and the more exact analytical results have been obtained by the application of those correction values.

II. Vapor pressure of the system, Na_2SO_4-H_2SO_4-H_2O

In the gas-volumetric analysis of soda ash, 30 per cent sulfuric acid is used customarily, in which sodium sulfate, produced by the interaction of soda ash and sulfuric acid, is dissolved and the vapor pressure of the solution will be changed. It is necessary to know the vapor pressure value of a solution, consisted of a mixture of free sulfuric acid and sodium sulfate, in the ratio of wide range to make proper correction. By using the simple apparatus described below, the vapor pressures of many sulfuric acid solutions containing different amount of sodium sulfate were measured at 10~30°C.

Measuring Method and Apparatus

The accuracy of the vapor pressuse necessary for the correction would be sufficient with 1/10 mmHg order. For quick and easy measurement of the vapor pressure having the above accuracy an apparatus shown in Fig. 1 was used, in which the increase of volume of a definite amount of dry gas caused by saturation with vapor by contacting with a solution to be measured was measured, from

(1) Brubacker, Ind. Eng. Chem., **7** (1915), 432 and others.

which the vapor pressure was calculated. The whole apparatus except the connecting capillary tube *C*, was immersed in a thermostat. The inner volume of the mercury burette *A* was 40 cc and that of bulb *d* of the measuring part *B* was almost equal. A micro burette *e* having inner volume of 2 cc and 0.01 cc graduation was attached to the lower part of *d*, by which the volume-increment of the gas phase was measured at the accuracy of 0.002 cc.

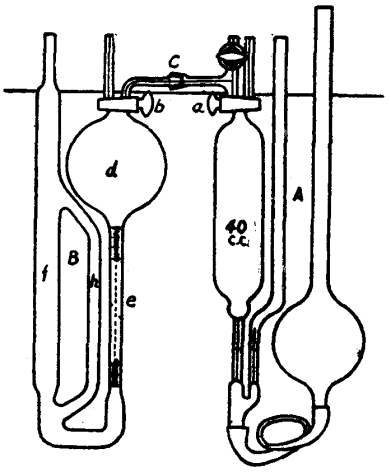

Fig. 1.

For the measurement, about 50 cc of the solution to be measured are introduced into *B* part from the upper part of *f* and then the parts of *d* and *e* are filled with the solution by sucking it through two way cock *b*. A definite amount of dry air taken into the burette *A* is transferred into *d* through *b*. The volum of the air is increased by water vapor and saturated with it within a few minutes, by which the solution is depressed into *e* part. Regulating the amount of the solution by drawing in or off the solution by means of a long pipette through the mouth of *f*, the levels of which in *e* and *h* are made coincidental, the pressure in the apparatus is made equivalent with the atmospheric pressure and the increase of the volume of the air is read.

Assuming air to be an ideal gas, the vapor pressure was calculated from the increase of gas volume using the formula : $p=P_2(1-V_1/V_2\cdot P_1/P_2\cdot T_2/T_1)$. Here, V_1 shows the volume of air taken into the burette *A* and V_2 the sum of V_1 and the volume increment of air. P_1 and P_2 show the atmospheric pressures measured at *A* and *B*, and generally $P_1=P_2$. T_1 and T_2 are the absolute temperatures at each time and $T_1=T_2$ when the thermostat kept well. In these cases, the vapor pressure is given with the formula : $p=P(1-V_1/V_2)$. When the experimental errors of *P*, *V* and *T* are in the ranges of 0.03 mmHg, 0.02 cc and 0.01°C respectively, the maximum error introduced by the above formula is 0.09 mm. The inner volume of the connecting capillary tube *C* out of the thermostat is about 0.2 cc and the error due to the temperature change is negligible.

The air for the experiment was stocked in a 5-liter air reservoir introducing through a calcium chloride tube and used for the measurement after passing over solid potassium hydroxide and phosphorous pentoxide. The solution for the measurement was kept in a thermostat for about 20 minutes, well shaken, and brought to equilibrium with the atmosphere at the temperature preventing dissolution or evolution of the air to the solution.

For assuring the accuracy of the measurement by the apparatus, the vapor pressure of distilled water was measured at 10~27°C, finding that the result was coincidental with Holbon's value in the mean error of 0.03 mm and the maximum one 0.08 mm. It was, therfore, concluded that the vapor pressure measurement

using the apparatus would be conducted in the accuracy of 0.1 mm.

The solution for the measurement was prepared at desired ratio by mixing an aqueous solution of sodium sulfate, concentration of which being 30 per cent calculated as sulfuric acid, and a 30 per cent sulfuric acid. The concentration of sodium sulfate in the solution for the measurement was determined by calculation, measuring sulfate radical as barium sulfate and the free acid by titration with potassium hydroxide.

Experimental results

The analytical results of each solution and the measured values of their vapor pressure are shown in Table 1. These results of each solution are expressed as follows:

No. 1 $\log p = 8.9574 - 2297.9/T$ (1)

No. 2 $\log p = 9.0467 - 3219.5/T$ (2)

No. 3 $\log p = 9.0345 - 2311.0/T$ (3)

No. 4 $\log p = 9.0290 - 2305.2/T$ (4)

Table 1. Measured Value of Vapor Pressure of the System Na_2SO_4-H_2SO_4-H_2O

No. and Composition of the Solution	Temp. (°C)	Pressure (mmHg) Observed	Calculated	No. and Composition of the Solution	Temp. (°C)	Pressure (mmHg) Observed	Calculated
No. 1	10.93	7.37	7.39	No. 3	10.58	7.74	7.75
	14.35	9.24	9.22		12.84	8.97	8.99
H_2SO_4 : 7.483N	17.70	11.38	11.40		15.04	10.42	10.37
	20.97	14.04	13.95	H_2SO_4 : 4.940N	16.59	11.41	11.37
Na_2SO_4: 0.000N	23.96	16.67	16.72		18.80	13.18	13.15
	27.58	20.69	20.72	Na_2SO_4: 2.553N	20.45	14.52	14.57
					22.62	16.60	16.64
	10.95	7.63	7.62		24.88	19.11	19.07
No 2.	12.34	8.36	8.36		28.09	23.10	23.07
	14.83	9.82	9.82				
H_2SO_4 : 6.204N	17.41	11.55	11.58	No. 4	12.56	9.13	9.13
	20.63	14.15	14.16		14.35	10.21	10.25
Na_2SO_4: 1.288N	20.79	14.32	14.29	H_2SO_4 : 3.706N	16.17	11.56	11.52
	24.13	17.56	17.55		19.60	14.25	14.28
	27.41	21.35	21.35	Na_2SO_4: 3.776N	22.45	17.08	17.00
					25.16	20.03	20.01
					28.24	23.93	24.00

The values calculated from these formulas are shown in the last column in the Table, which shows that the difference between the observed values and the calculated one lie within experimental error. It was known from these results that the vapor pressure increased as sodium radical increased when the concentrations of sulfate radicals were coincident. But as the range of measured temperature was narrow and the accuracy of vapor pressure was about 0.1 mm, the change of the vapor pressure against that of the concentration ratio was compartively small comparing with the experimental error. It was, therefore, difficult to make clear the relation between the coefficient of the experimental formnla and the concentration. The vapor pressure at each concentration obtained graphically using the table 1, were shown in Table 2.

Table 2. Vapor pressure of the system Na_2SO_4-H_2SO_4-H_2O (mmHg)

Conc. of Na (N)	10°C	15°C	20°C	25°C	30°C
0.00N	6.95	9.60	13.15	17.79	23.82
0.50 "	7.03	9.70	13.35	18.06	24.23
1.00 "	7.12	9.87	13.54	18.35	24.63
1.50 "	7.21	10.01	13.73	18.63	25.01
2.00 "	7.30	10.15	13.93	18.91	25.39
2.50 "	7.41	10.30	14.13	19.18	25.75
3.00 "	7.52	10.46	14.33	19.44	26.08
3.50 "	7.64	10.62	14.52	19.69	26.40

Concentration of sulfate radical: 7.49N

III. Solubilty of carbon dioxide

In the gas-volumetric analysis of carbonates, the correction on the solubility of carbon dioxide is more important than that on the vapor pressure. As no applicable value for this purpose was found in the literature, it was measuaed at 15 ~30°C by changing the concentration of sodium radical keeping that of sulfate radical at almost constant.

Measuring method and apparatus

In the present measurement, carbon dioxide produced by adding 30 per cent sulfuric acid on anhydrous sodium carbonate was dissolved in its solution and its solubility was determined by analyzing the solution. The experimental apparatuses are shown in Fig. 2. In the apparatus I, inner volume of *A* is 80 cc and that of *B* 120 cc. A proper amount of anhydrous sodium carbonate was introduced into *A* and 100 cc of 30 per cent sulfuric acid into *B*. After exhausting air in the apparatus a drop of sulfuric acid was dropped upon sodium carbonate producing carbon dioxide, which was then exhausted. By repeating the process several times, the air in the apparatus was replaced with carbon dioxide. Then the whole apparatus was immersed into a thermostat and sulfuric acid was gradually dropped on the carbonate under shaking. The evolved carbon dioxide gas entered into *B* from the bottom through the side tube and out to the atmosphere through liquid paraffin trap after passing in the bubble state and dissolving in the solution. Regulating the adding velocity of the acid to make complete addition before ceasing the evolution of carbon dioxide gas, perfect saturation of the gas was obtained. After complete decomposition of the carbonate, the apparatus was shaken for 20~30 minutes in the thermostat obtaining perfect equilibrium. Then cocks *b* and *c* were closed and the apparatus was taken out from thermostat. *A* part was quickly removed from the

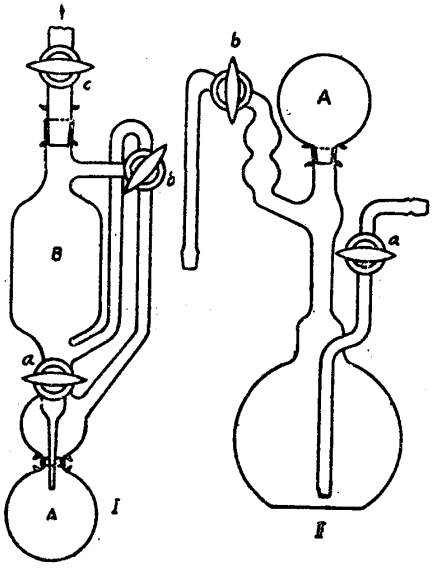

Fig. 2.

apparatus and fixed to the upper part of II. As the inner diameter of the connecting part of *A* is about 4 mm and very small comparing with the inner volume of *A* (80 cc), errors due to the loss of dissolved carbon dioxide by exposing to air and to the temperature change might be negligible. The temperature change of the thermostat during the experiment was 0.05~0.03°C.

As a large amount of carbon dioxide was evolved from the solution itself, remained air, if any, was almost replaced with the dioxide and the gas phase was completely composed with carbon dioxide. The presence of other gas was a cause of error, which was not, however, taken into consideration in this case from the above reason.

The dissolved amount of carbon dioxide and the composition of the solution were determined by analyzing the solution in *A* at the upper part of II, which was moved to the lower part by shaking the apparatus, closing two cocks *a* and *b*. Carbon dioxide dissolved in the solution was driven off by CO_2-free air introduced from *a* and the gas was absorbed in an absorbing solution attached to *b*. As the absorbing solution, a definite amount of 0.1~0.25 N potassium hydroxide solution was used according to the amount of the dioxide. A trap containing barium hydroxide solution was attached to the absorption apparatus for confirming the perfect absorption. Barium chloride was added to the solution absorbed carbon dioxide. Barinm carbonate produced was filtered off and the amount of carbon dioxide was determined by titrating the filtrate with hydrochloric acid. The result was corrected by comparing with that of a blank test conducted in parrllel. The solution from which carbon dioxide was driven off was diluted and the sulfate radical in it was determined as barium sulfate, sulfuric acid with potassium hydroxide and sodium sulfate by the difference.

Results

The results obtained at 15, 20, 25 and 30°C are shown in Table 3 and Fig. 3. The pressure of carbon dioxide at equilibrium was corrected using the above observed values and the solubility of carbon dioxide was calculated as that at 1 atmospheric pressure assuming its complying with Henry's law. Fig. 3 expresses the relation between the solubility of corbon dioxide and the concentration of sodium radical, which shows that four isothermal lines are almost straight lines though the concentrations of sulfate radicals are not always same. When the solubility is assumed to expressed with the following formula,

$$S_{CO_2} = (a_0 + b_0\theta + c_0\theta^2) - C_{Na}(a_1 + b_1\theta + c_1\theta^2) - a_2C_{SO_4},$$

then S_{CO_2} is expressed as follows:

$$S_{CO_2} = (0.9527 - 0.01843\theta + 0.0^4925_3\theta^2) - C_{Na}(0.1533 - 0.002518\theta - 0.0^5348_7\theta^2) + 0.00537_7C_{SO_4} \quad (5)$$

Here, S_{CO_2} expresses Bunsen's absorption coefficient, C_{Na} and C_{SO_4} the concentrations of sodium and sulfate radicals respectively expressed with their normality and θ the temperature at Celsius scale. Values calculated using the formula (5) are shown at the last column of Table 3; the difference betwwn the calculated values

Table 3. Observed Value of Solibility of Carbon Dioxide

Temp. (°C)	Composition of the Solution (N)			Solubility of CO_2 (cc/cc)*	
	H_2SO_4	Na_2SO_4	Total SO_4	Obs.	Calc.
15.00±0.05	4.097	2.974	7.072	0.394	0.394
"	4.560	2.575	7.135	0.440	0.440
"	5.403	1.787	7.191	0.532	0.531
"	6.199	1.049	7.248	0.616	0.616
20.00±0.05	4.034	2.956	6.990	0.357	0.357
"	4.240	2.991	7.231	0.354	0.356
"	4.382	2.649	7.031	0.390	0.390
"	5.365	1.942	7.307	0.464	0.463
"	5.796	1.586	7.382	0.497	0.500
"	5.937	1.439	7.376	0.513	0.515
"	6.228	1.153	7.381	0.543	0.544
25.00±0.03	4.116	3.096	7.213	0.317	0.316
"	4.162	3.045	7.207	0.320	0.320
"	4.632	2.611	7.243	0.360	0.358
"	4.994	2.246	7.240	0.391	0.391
"	5.544	1.766	7.310	0.434	0.433
"	6.045	1.278	7.323	0.477	0.476
"	6.161	1.239	7.340	0.480	0.480
30.00±0.03	4.279	2.890	7.169	0.304	0.306
"	4.992	2.244	7.237	0.355	0.354
"	5.721	1.591	7.312	0.404	0.404
"	6.047	1.267	7.315	0.426	0.428

* Bunsen's absorption coefficient

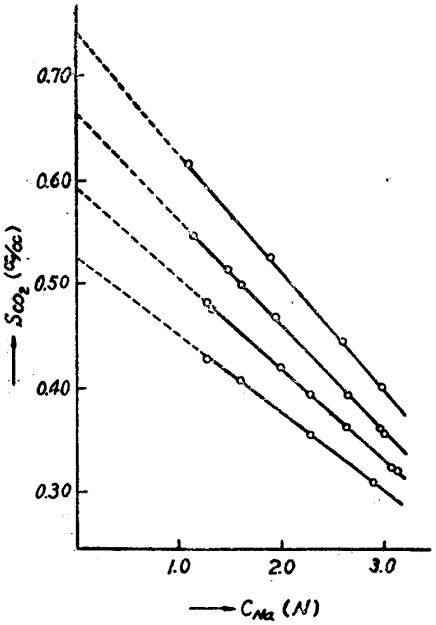

Fig. 3.

and the obseved ones is 0.6 per cent at the maximum and 0.3 per cent the mean.

It is noticed at the formula (5) that the coefficient of C_{SO_4} is small and positive sign, which means that the increase of sulfate radical increases the solubility of carbon dioxide though small, in the present experimental range. As the change of the sulfate radical concentration is small from the essential purpose of the present work and its coefficient is very smaller than that of C_{Na}, the term may be taken as a conctant. It has been known that the solubility of carbon dioxide in sulfuric acid has a minimum value at a certain concentration of the acid[2]. At the present measurement, the minimum point is supposed to lie near the measured concentration of the acid and to move by the influence of sodium radical. From these facts, it is supposed that the term of C_{SO_4} become constant. But no definite conclusion was obtained owing to the narrow range of the measured

Table 4. Solubility Table of Carbon Dioxide for the Correction of Gas-Analysis (cc/cc)*

Temp. (°C)	Conc. of sodium radical (N)			
	0.00	1.00	2.00	3.00
10	0.818	0.690	0.562	0.434
12	0.785	0.662	0.539	0.416
14	0.753	0.635	0.518	0.400
16	0.721	0.609	0.497	0.384
18	0.691	0.584	0.477	0.370
20	0.661	0.559	0.457	0.356
22	0.632	0.535	0.439	0.343
24	0.604	0.512	0.421	0.330
26	0.576	0.490	0.405	0.319
28	0.549	0.469	0.388	0.308
30	0.523	0.448	0.373	0.298

* Bunsen's absorption coefficient
Concentration of the used sulfuric acid : 7.49N

(2) A. Christoff, Z. physik. Chem., **53** (1905), 321.

temperature, concentration, and experimental error.

For convenience to apply the correction to analysis, the correction values at each concentration of sodium radical and each temperature calculated from the formula (5) are shown in Table 4.

IV. Analytical examples

1. Sodium carbonate

The above correction was applied to the gas-volumetric analysis of carbonate as an example. In the gas-volumetric analysis, the state is not always considered to be same with the equilibrium state at which the correction was obtained, but it is clear that there is some deviation according to an apparatus used and experimental conditions[3]. For minimizing the deviation, the following analytical apparatuses have been used. As the correction for the amount of corbon dioxide caused by the dissolution should be precise, it is desirable that the gas phase contacting with the decomposed solution of the carbonate should be exclusively carbon dioxide. For the purpose, apparatuses show in Fig. 4 *A* and *B* have been used, in which the volume of the gas phase was designed to be vary small comparing with that of the evolved carbon dioxide. In *A*, the volume of *a* is almost same (2~4 cc). A solid sample is put in *a* and a definite amount of 30 per cent sulfuric acid in *b* and connected to a mercury gas burette (with water jacket to keep the temperature constant). Shaking and rotating the connecting part, the acid in *b* is gradually dropped into *a*. In *B*, a solid sample is gradually dropped into the acid. At the middle of the cock, a hollow of 0.5~1 cc is made, in which solid sample is put. A channel is made around the cock so that gas phase can be connected between *d* and *e* in spite of the direction of the cock. In each apparatus, the correction values at equilibrium were assumed to be applied without modifying them. The mean value of the first and last vapor paessure was adopted as its value. To calculate the composition of the solution, the sample of sodium carbonte was taken to be pure.

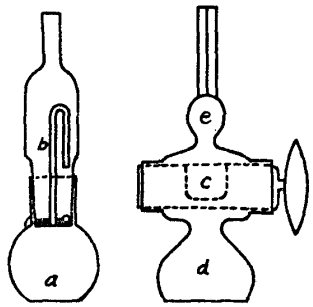

Fig. 4.

Analytical examples are shown in Table 5. Correction values were adopted from

Table 5. Analytical Examples of Sodium Carbonate

No.	Sample (mg)	30%H_2SO_4 (cc)	Evolved CO_2 (cc at N.T.P.)	Dissolved CO_2 (cc)	Vapor Press. (mmHg)	Corrected Vol. of CO_2 (cc)	Na_2CO_3 %
A-1	240.7	2.0	49.61	1.15	6.0	50.36	99.6
A-2	289.9	2.0	60.30	0.93	7.5	60.63	99.6
B-3	229.2	2.0	47.49	1.08	7.3	48.10	100.0
B-4	236.3	2.0	48.94	1.10	6.9	49.58	99.9
B-5	227.5	2.0	47.05	1.10	6.2	47.76	100.0

(3) Hata, J. Soc. Chem. Ind. Japan, 36 (1933), 1.

the data in Tables 2 and 3. The samples *A*-1 and *A*-2 were prepared by heating recrystallized chemically pure sodium carbonate and *B*-3, *B*-4, and *B*-5 by drying the *A*-sample until getting constant weight. The analytical error was assumed to be less than 0.1 per cent.

2. Calcium carbonate

The gas-volumetric analysis of calcium carbonate can be realized as in case of sodium carbonate. It takes, however, longer experimental time for completing the reaction because calcium sulfate produced is precipitated. The correction value of calcium carbonate should be independently seeked for. But, it was supplemented with the value of solubility of carbon dioxide and vapor pressure of sulfuric acid solution neglecting the solubility of calcium sulfate in the acid. As no reliable solubility values of carbon dioxide in sulfuric acid of desirable concentration were found, they were diagrammatically assumed from the solubility of carbon dioxide in pure water and 30 per cent sulfuric acid at each temperature, using values at 15 and 25°C for 0~4 N sulfuric acid obtained by G. Geffecken[4] and those for 30 per cent sulf-uric acid calculated from the formula (5). The values were shown in Table 6.

Table 6. Solubility of Carbon Dioxide in Sulfuric Acid (cc/cc)*

Temp.	Concentration of H_2SO_4 (N)			
(°C)	5.0	6.0	7.0	7.45
10	0.861	0.838	0.822	0.818
12	0.824	0.803	0.789	0.785
14	0.787	0.768	0.756	0.753
16	0.749	0.733	0.723	0.721
18	0.715	0.700	0.692	0.691
20	0.682	0.677	0.662	0.661
22	0.649	0.638	0.634	0.634
24	0.618	0.608	0.604	0.604
26	0.588	0.579	0.576	0.576
28	0.558	0.550	0.549	0.549
30	0.532	0.525	0.523	0.523

* Bunsen's absorption coefficient

For the annlysis, the apparatus shown in Fig. 4-*B* was used. As the produced colloidal precipitate of calcium sulfate covered the surface of the sample, the carbonate was finely powdered and gradually added into sulfuric acid, by which the reaction was completed making the analysis possible. In this case, the proper amount of the sample per 1 cc sulfuric acid would be about 20~40 mg. When larger amount of the sample was used, the reaction became very slow, making the analysis difficult. The carbonate was completely decomposed in about 30 minutes, giving a definite value. Analytical examples are shown in Table 7. The samples C-1 and C-2 are chemically pure calcium carbonate, while D-3~6 powdered marble for producing carbon dioxide. As seen from the examples, the method may be applicable to the analysis in ±0.2 per cent error.

(4) G. Geffecken, Z. physik. Chem., **49** (1904), 257.

Table 7. Analytical Examples of Calcium Carbonate

No.	Sample (mg)	30%H_2SO_4 (cc)	Evolved CO_2 (cc at N.T.P.)	Dissolved CO_2 (cc)	Vapor Press. (mmHg)	Corrected Vol. of CO_2 (cc)	$CaCO_3$ %
C-1	160.5	5.0	32.48	3.71	10.0	35.71	100.1
C-2	165.3	5.0	33.60	3.71	10.0	36.82	100.2
D-3	251.0	5.0	52.36	3.87	9.0	55.52	99.5
D-4	154.0	5.0	30.41	3.95	8.2	33.99	99.3
D-5	168.1	5.0	33.92	3.77	9.7	37.21	99.6
D-6	178.7	5.0	36.71	3.44	12.2	39.49	99.4

Summary

(1) The vapor pressure of the system, Na_2SO_4-H_2SO_4-H_2O was measured using a simple apparatus.

(2) The solubility of carbon dioxide in the system was measured.

(3) By improving a gas-volumetric analytical apparatus, the correction value became easily applicable. Moreover, the gas-volumetric analysis of sodium carbonate was conducted with good result by applying the correction above obtained.

(4) The analytical condition of calcium carbonate by the same method was obtained and it was shown that the process was conducted in 0.2 per cent error.